Rate of Growth of Crystals In Aqueous Solution

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A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Michigan.

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Rate of Growth of Crystals in Aqueous Solution[1,2]

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A new apparatus has been designed and a new method has been developed for the study of continuous crystallization of aqueous solutions.

The action of sodium sulfate and magnesium sulfate in the continuous crystallizer has been studied quantitatively in the temperature range of 27° to 31° C. It has been shown that there is a definite relation between the weight of material crystallized and the new surface generated during that crystallization under definite conditions of concentration changes. The probable effects of variation of this relation due to changes in temperature and viscosity have been indicated.

A method for the application of the data on the variation of weight and surface of crystals under given conditions to the prediction of the approximate size of product has been devised.

CRYSTALLIZATION in commercial practice is conducted in two principal ways. The first is the older method of allowing a batch of strong, hot solution to crystallize by slow cooling. The second and newer method consists of continuous cooling of a stream of hot solution with agitation so that the crystals are held in suspension until the magma leaves the apparatus. In attempting to design crystallizers for this method it was found that very

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little was known about the actual rate of growth of crystals and this investigation marked the beginning of an attempt to supply that information.

Previous Work

There is considerable work described in the literature on the mechanism of the formation of crystal nuclei. A useful picture of the origin of such crystals has been given by Von Weimarn.[3] He assumes that molecules, moving in the solution under the influence of convection currents or artificial agitation, form at intervals larger collections of molecules whose existence in unsaturated and saturated solutions is only momentary. Link[4] thought he could detect such nuclei at the moment of separation.

Von Weimarn further states that, since very small particles of any substance are always more soluble than larger particles, one must assume that, even in solutions supersaturated to a limited extent, the existence of collections of molecules is transitory. With increasing supersaturation of the solution the concentration would be such as to be in equilibrium with the largest of these aggregates. They become stabilized and at intervals become larger by the addition of new molecules. Owing to this growth the solubility of the particles decreases rapidly and the surrounding solution becomes very strongly supersaturated by them. The formation of further crystal centers is hindered when the supersaturation has been depressed to a level corresponding to the unstable solid phase. As soon as the particles reach microscopic size the difference in solubility is usually inconsequential and there will exist only a small supersaturation to act as a driving force for further growth. The mechanical action of velocity is important here, because it hinders diffusion and, therefore, the rapid exchange of particles in the solution in the immediate neighborhood of the crystal. Jones and Partington[5] have given a mathematical discussion of the supersaturation theory which agrees in principle with the above. An idea of the necessary size of such particles is obtained from the observations of Ostwald[6] that in a saturated solution of sodium chlorate 10^{-9} gram was capable of crystal formation. This corresponds to a radius of 10 microns. McIntosh[7] says that the weight of particles which induce crystallization of supersaturated solutions of sodium sulfate were found to be 10^{-13} to 10^{-18} gram in one case and 10^{-12} to 10^{-14} in another.

There has been a considerable discussion as to whether or not a crystal nucleus could form spontaneously, and no definite conclusion has yet been reached.

Some work has been done on the rate of crystal growth after nuclei have been formed. Le Blanc[8] studied the rate of crystallization of potassium dichromate in aqueous solution. The velocity of crystallization was calculated from the equation

$$\frac{dx}{dt} = KS(C_2 - C_1)$$

where dx/dt is the rate of increase of weight, S is the surface exposed, C_2 is the concentration of the saturated solution, and C_1 is the average concentration of the supersaturated solution.

A considerable amount of work was done by Marc.[9] He inoculated a supersaturated solution of potassium sulfate with very fine seed crystals, keeping the solution rapidly stirred.

[3] "States of Matter," pp. 40, 150 (1914).

[4] *Pogg. Ann.*, **46**, 258 (1839).

[5] *Z. physik. Chem.*, **88**, 291 (1914).

[6] "Lehrbuch der allgemeinen Chemie," Vol. II, 2nd ed., p. 754.

[7] *Trans. Roy. Soc. Can.*, **III, 13**, 265 (1919).

[8] *Z. physik. Chem.*, **77**, 614 (1911).

[9] *Ibid.*, **61**, 385 (1907); **67**, 470, 640 (1908); **68**, 104 (1908); **73**, 685 (1909).

Under these circumstances the velocity of crystallization appeared to follow the laws of a reaction of the second order. He first used the equation given by Le Blanc above, and later modified it to conform to a second order equation.

Marc's work has been criticized by Wagner,[10] the discussion centering largely on the calculation of surface area. Jenkins[11] carried on similar work, which is mentioned later in this article.

The principal difficulty with Marc's work is that his values for K vary over a considerable range. Campbell[12] has shown that it is almost impossible for two crystals to grow at the same rate even when they are symmetrically placed in a solution, whereas Marc assumed that all the crystals grew at the same rate.

Kucharenko[13] has investigated the crystallization of sucrose. He experimented with large, individual, perfect crystals in solutions of known degree of supersaturation. He expressed his results in terms of increase in weight in milligrams per square meter per minute and found that this rate of growth varied with temperature, velocity, and degree of saturation. If these were all kept constant, an equal rate of growth per unit of surface would mean that a large crystal would increase more in absolute weight but less in relative weight than a small one. Kucharenko's work, though very extensive, is not strictly comparable with the problem in hand, because supersaturated sucrose solutions are easily prepared and their degree of supersaturation may be measured; whereas this is not true of ordinary inorganic solutions.

EXPERIMENTAL

It would therefore seem desirable to determine the rate at which a crystal of some common inorganic substance would grow when kept in suspension in a moving solution which was at the same time being cooled regularly. Because it would be difficult to accomplish this with a single crystal of considerable size, it was decided to work with a large number of crystals of known size and to determine the factors affecting their rate of growth.

Description of Apparatus

The apparatus, all stationary parts of which are of glass, is shown in Figures 1 and 2. It consists of a saturator, A, nearly filled with crystals, through which heated, undersaturated liquid passes downward to make as long a path as possible to the outlet of the vessel, which is surrounded by a 40-mesh monel metal screen, U. The temperature of the liquid in A is maintained by the hot-point immersion heater, H_1, of 500 watts capacity, which is controlled by the thermostat T_1 in the mixing vessel B. The temperature of the saturated solution leaving A and being siphoned into B is kept about as high as desired in C. The mixing vessel B provides a supply of slightly supersaturated solution to the vessel C. The temperature of the liquid in B is held constant by the 60-watt heater H_2 in circuit with the thermostat T_1. The liquid in B is agitated by the stirrer L. The

[10] *Ibid.*, **71**, 401 (1910); *Z. Elektrochem.*, **17**, 989 (1911).
[11] *J. Am. Chem. Soc.*, **47**, 903 (1925).
[12] *J. Chem. Soc. (London)*, **107T**, 475 (1915).
[13] *Louisiana Planter*, **71**, 211, 231 (1923).

liquid from B passes through a fine-mesh cloth filter at J, to prevent any chance introduction of nuclei.

The vessel C is heated by the 60-watt heater H_3 controlled by the thermostat T_2. The liquid is agitated by the stirrer L, and the temperature is held at such a point that crystallization barely starts before the nuclei enter the crystallizer proper, D. A weighed number of sized seed crystals are added to C every 5 minutes. The crystallizer D is a 3-inch (76-mm.) Pyrex tube about 5.5 feet (1.7 meters) long, set with a slope of 1 inch (25 mm.) throughout its length. The ends of the tube are closed by brass plates held in place by four steel tension rods $^3/_{16}$ inch (4 mm.) in diameter. The nuclei are kept suspended in the solution by the agitation produced by a spiral stirrer of copper and brass. This stirrer is smaller in diameter than the tube, and is finished with a 0.5-inch (13-mm.) rubber ribbon which on turning maintains continuous contact with the Pyrex tube. The ribbon itself makes two turns in 5 feet (1.7 meters). Attrition is almost entirely prevented by the use of the flexible rubber ribbon while at the same time effective agitation is produced. The shaft of the stirrer is supported by bearings in each of the brass plates at the ends of the tube and by a specially constructed central bearing held in place by brass spring clips.

The temperature of the crystallizer is maintained by blowing compressed air of suitable temperature between the outer wall of the tube and the air jacket F, as it is necessary to cool the solution slowly and uniformly and to avoid local cooling. The spiral stirrer, which was revolved by a motor, M, acting through a speed reducer, G, was turned at 9.5 to 12 r. p. m., and not only agitated the solution but also slowly conveyed the growing crystals to the discharge pipe at O. A salt leg was provided at O by means of large-size glass and rubber tubing. The clamps K_1 and K_2 allowed the easy removal of the crystalline material.

The impoverished solution flowed from the top of the tube to the outlet pipe, Y, which was provided with a resistance heater of 150 watts capacity, H_4. The temperature of the heater was regulated by the lamp-bank resistance R_2 in parallel with the slide-wire resistance R_1. This method of heating immediately after the solution had left the crystallizer prevented any stoppage in the return line and insured smooth operation of the Pyrex pump P. This pump was a single-cylinder reciprocating pump, operated by an adjustable eccentric, E, rotated by a moto , M. A cone pulley on an intermediate shaft driven by the motor allowed a speed variation in individual runs such as to produce a pump discharge of from 125 to over 200 cc. o solution a minute. The piston consisted of a rubber cylinder held in place on the piston rod by brass rings. The valve seats were rubber cylinders with openings controlled by glass ball valves. It was found after adjustments had been made

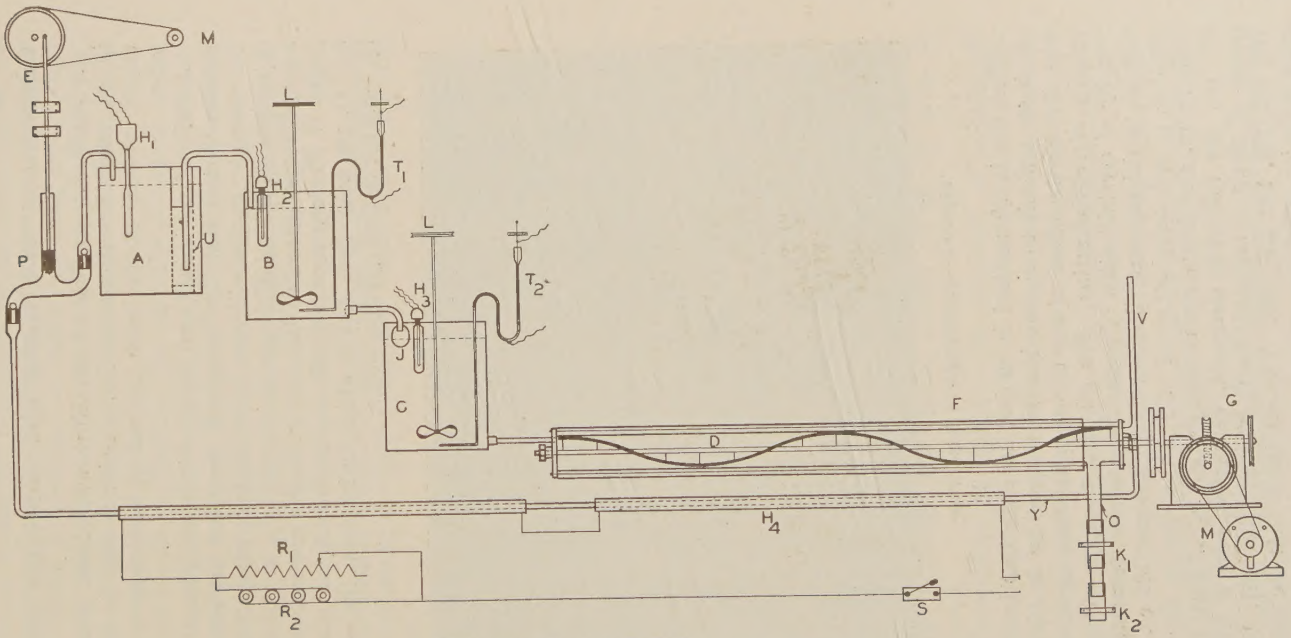

DIAGRAM OF APPARATUS

Figure 1

that very uniform flow of solution could be maintained with this pump.

Comparison of Batch Method with Continuous Method

A continuous method of procedure was chosen because in this method constant terminal conditions may be maintained, whereas in the batch method all conditions would vary.

A series of preliminary experiments in a small batch apparatus showed that this theoretical reasoning was correct. For example, results with the batch method, using 3 liters of sodium sulfate solution saturated at 30° C., stirred with a propeller-type stirrer at 160 r. p. m. in the presence of 10 grams of 35-mesh seed crystals and cooled at the rate of 0.5° C. per hour, gave results which varied from the mean by −8.8 per cent to +5.9 per cent.

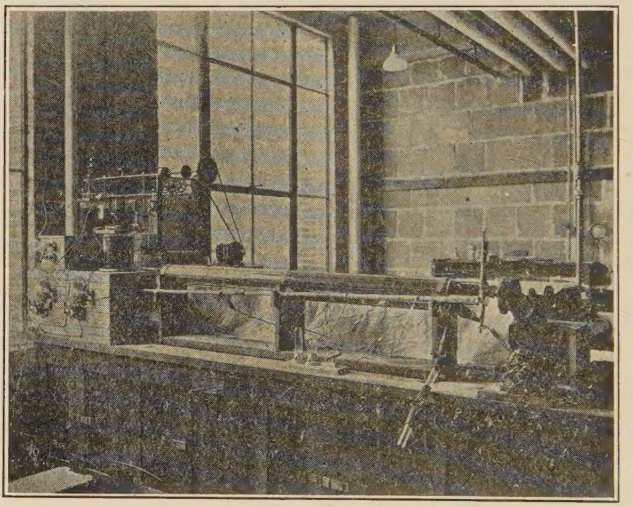

Figure 2—Photograph of Apparatus

That the batch method is subject to variations in rate which are difficult to control has been shown by Jenkins,[14] who studied the effect of initial supersaturation upon the velocity of crystallization. His calculation of the average velocity of crystallization of ammonium nitrate shows that with an initial supersaturation of 1.00 gram per 100 cc. of solution, a bath temperature of 0.10° C., a stirring rate of 1000 r. p. m., and an amount of seed crystals of 1.0 gram per 100 cc., the following constants, calculated over a total period of about 2 minutes, were obtained: 162, 161, 168, 176, 166, 163, 162, 152, 160. The average is 164; the maximum deviation, ±7.9 per cent.

[14] *J. Am. Chem. Soc.*, **47**, 903 (1925).

Materials

Sodium sulfate and magnesium sulfate were prepared for use by dissolving the commercial salts in water, aerating at the boiling temperature to oxidize any iron present, and filtering with Filter-cel to remove any suspended solid material. From the clear solutions thus obtained the material was recrystallized for use.

PROPERTIES OF Na_2SO_4—The solubility of sodium sulfate in the range of 20° to 32° C. was taken from the recently determined values of Richards.[15] The following equation expressed the solubility relation very closely:

Let X = grams Na_2SO_4 per 100 grams of solution, and t = temperature in degrees Centigrade. Then

$$X = 10.102 - 0.37145t + 0.0335t^2 \qquad (1)$$

The density values of sodium sulfate solutions were taken from those of the Earl of Berkeley[16] and Dawson and Williams.[17]

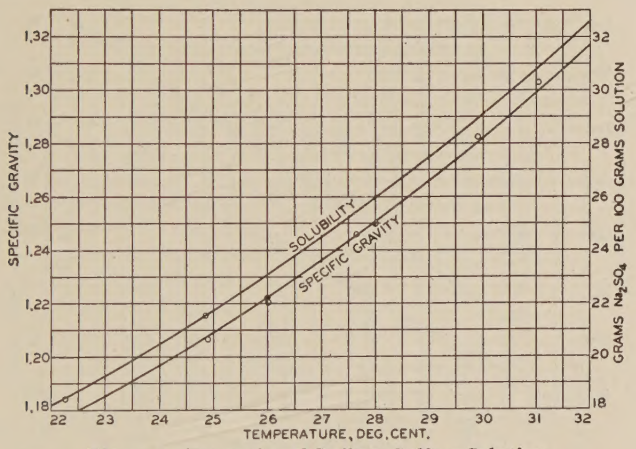

Figure 3—Properties of Sodium Sulfate Solution

The solubility and specific gravity curves are given in Figure 3.

PROPERTIES OF $MgSO_4$—The solubility of magnesium sulfate in the range 0° to 40° C. was taken from Landolt-Börnstein Tabellen.[18] The following equation was found to express the solubility relation closely, except at 25° C.:

Let X = grams $MgSO_4$ per 100 grams of solution, and t = temperature in degrees Centigrade. Then

$$X = 20.5726 + 0.29461t - 0.0006602t^2 \qquad (2)$$

The density values of magnesium sulfate solutions were those of Barnes and Scott.[19]

[15] *J. Am. Chem. Soc.*, **40**, 164 (1918).

[16] Seidell, Table of Solubilities of Inorganic and Organic Compounds, 2nd ed., p. 667.

[17] *J. Phys. Chem.*, **4**, 370 (1900).

[18] Tabellen, Vol. I, p. 666 (1923).

[19] *J. Phys. Chem.*, **2**, 542 (1898).

The data followed a linear relation quite closely and could be expressed by the equation (3).

$$X = 1.2216 + 0.00347t, \text{ where } t \text{ is the temperature} \qquad (3)$$

The solubility and specific gravity curves are given in Figure 4.

Preparation of Seed Crystals

Seed crystals were prepared by using the material which passed through a 28-mesh and was retained on a 35-mesh Tyler standard screen. In these screens the successive openings have a ratio of $\frac{1.414}{1} = \frac{\sqrt{2}}{1}$, so that each successive area of opening is double that of the preceding one. The material retained on a 35-mesh screen was assumed to have the average diameter between 28 and 35 mesh of 0.0198 inch (0.0503 cm.).

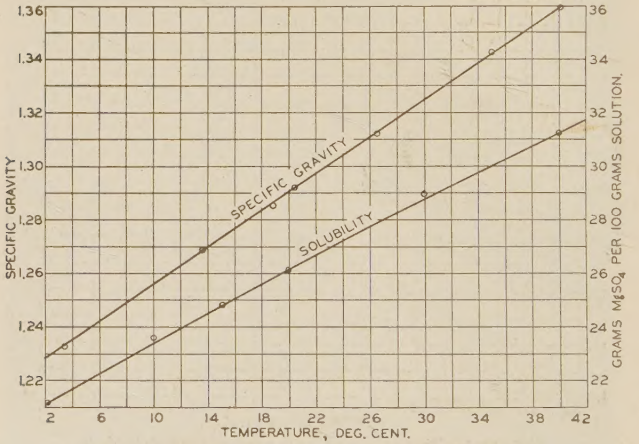

Figure 4—Properties of Magnesium Sulfate Solutions

In this way by a careful screen sizing, eliminating all dust as far as possible, seed crystals were prepared and kept in tightly stoppered test tubes.

Procedure

The apparatus was flushed with distilled water at the beginning of each run. The whole system was then filled with saturated solution, previously prepared, which had been superheated about 5° or 6° C. above its crystallization point. The saturator was filled with crystalline material and thermometers reading to 0.02° C. were placed in the saturator outlet, the seed crystal vessel, and in the exit tube from the crystallizer. The pump was then started to circulate the solution, and the stirrers, together with the spiral agitator, gave sufficient mixing to insure uniform conditions throughout the apparatus. By means of the heaters acting

Table I—Data Sheet for Run 15

Time	Temperatures		Flow	Seed Crystals Added	Yield of Salt $Na_2SO_4.10H_2O$	Screen Test of Final Product	
	Saturator exit	Crystallizer exit					
	° C.	*° C.*	*Cc. per min.*			*Mesh*	*% by wt.*
10:30	27.14	28.16	10:32 = 124	10:20 start tube *A*			
10:45	27.04	27.54		50 grams		10	1.16
11:00	27.01	27.05	11:03 = 138		11:12 start	14	23.94
11:15	27.15	26.85				20	41.30
11:30	27.04	26.84	11:40 = 116			28	27.90
11:45	27.12	26.85		11:45 start tube *B*		35	4.10
12:00	27.08	26.86	12:20 = 122	52.9 grams	12:00 took 1 leg salt	48	1.00
12:15	27.20	26.86				65	0.60
12:30	27.02	26.87			12:30 took 1 leg salt		100.00
12:45	27.19	26.92	12:50 = 124				
1:00	27.01	26.96			1:05 took 1 leg salt		
1:15	27.20	26.99	1:10 = 115	1:10 start tube *C* 12.8 gram			
1:30	27.24	27.03		13:0 stop tube *C*	1:35 took 1 leg salt		
Average	27.125	26.90	123 cc.	36.5 grams per hour			
Corrected temperature	27.125	26.85					

in conjunction with the thermostats, the temperatures of the apparatus and the solution were gradually brought to their desired values. This preliminary period during which no data were taken usually took an hour or more. When conditions were constant and the correct temperatures were obtained, a measured volume of seed crystals was added every 5 minutes to the seed crystal vessel. Thermometer readings were made every 5 minutes to insure accurate control while readings were recorded every 15 minutes. The pump discharge in cubic centimeters per minute was taken every half hour. By the use of Pyrex tubes the course of the crystallization could be observed at every point. A visual increase in size of crystals between the inlet and outlet could readily be observed. The spiral agitator with its rubber ribbon kept the crystals almost continuously suspended in the solution so that the entire tube when sufficiently well illuminated gave the appearance of a heavy snowstorm of crystals. As soon as the salt leg was filled with crystals, it was emptied and the time noted.

The solid material was covered so that no water of crystallization would be lost and placed on a suction filter to drain. Usually a run was made over a period of about 3 hours and the product saved for that length of time.

The solution from the exit of the crystallizer was continuously heated and pumped back to the saturator and brought back to its normal concentration to be used again in the cycle.

Screen Analysis of Product

The crystalline material, after being removed from the salt leg, was placed on a suction filter to remove as much adhering liquid as possible. It was then dried in a controlled humidity drier to avoid loss of water of crystallization.

In the work on $MgSO_4.7H_2O$ it was found that washing the crystals with ethyl alcohol that had been previously saturated with magnesium sulfate washed away any small amount of adhering mother liquor and cut down the time of drying considerably.

The resulting material was then weighed and carefully screened and the portions retained on each screen were weighed to the second decimal place. In this way the distribution of sizes was obtained and the resulting screen analyses plotted. Table I shows a typical data sheet for run 15.

Typical Calculations for Run 15—In figuring seed crystal area the assumption has been made that there is a linear size distribution of particles between 35 mesh, opening 0.0417 cm., and 28 mesh, opening 0.0589 cm. The average size of particle retained on the 35-mesh screen is then taken as $\frac{0.0589 + 0.0417}{2}$, or 0.0503 cm. To obtain the relative change in surface between the seed crystals and the final product, the particles are assumed to be cubes.

This method of figuring surface changes from the screen test does not give absolute values, but it does give a reliable means of measuring the relative change in surface. The actual change in surface would then be equal to some constant times this calculated value, as long as the crystals grow symmetrically and are not distorted. It is known that in a continuous crystallizer, in which the seed crystals are kept gently in motion, the crystals do grow uniformly without distortion.

The number of particles per gram on any one screen—for example, 35 mesh—would be

$$\frac{1}{D^3 \times \text{density}} = N$$

Then $N \times 6 \times D^2$ = surface in square centimeters when D is in centimeters, and the density is expressed in grams per cubic centimeter. This surface in square centimeters per gram is equal to

$$\frac{1 \times 6 \times D^2}{D^3 \times \text{density}} \text{ or } \frac{1}{D \times \frac{\text{density}}{6}} = \frac{1}{0.2436\,D} \qquad (4)$$

The density of $Na_2SO_4.10H_2O$ is 1.462^{20} and $\frac{1.462}{6} = 0.2436$.

For 1 gram of 35-mesh material there would be $\frac{1}{0.2436 \times 0.0503}$ = 81.61 sq. cm. of surface. In the same way the number of square centimeters per gram of material retained on each screen was figured as given in Table II. The total surface in the final product was then figured as the sum of the individual surfaces.

Table II—Screen Test of Final Product
(Surface per 100 grams of product)

Retained on Mesh	Screen Test		Surface per Gram		Total Surface
	% by wt.		*Sq. cm.*		*Sq. cm.*
10	1.16	×	20.46	=	23.8
14	23.94	×	29.14	=	699.0
20	41.30	×	41.03	=	1693.0
28	27.90	×	57.73	=	1610.0
35	4.10	×	81.61	=	334.4
48	1.00	×	115.30	=	115.3
65	0.60	×	163.20	=	97.9
	100.00				4573.4

The yield of salt per hour may be figured from the concentration change and the rate of flow of solution. For example, the amount crystallized is

$$123 \times 60 \times 1.236 \times \frac{0.40}{100} \times \frac{322.2}{142.1} = 82.80 \text{ grams per hour}$$

Flow in cc. per minute × 60 minutes × the average specific gravity of solution × the concentration change per 100 grams of solution ÷ 100 × $\left(\frac{Na_2SO_4.10H_2O}{Na_2SO_4} = \frac{322.2}{142.1}\right)$ = yield per hour in grams. The total yield is the sum of the

[20] Landolt-Börnstein Tabellen, Vol. I, p. 303 (1923).

amount crystallized out plus the seed crystals added per hour, or 82.8 + 36.5 grams = 119.3 grams per hour.

Beginning with experiment 21 the yield was checked by actually weighing the total dried product. This was found to be more satisfactory. In run 15 checks on the inlet and outlet concentrations showed a change of 0.39 gram per 100 grams of solution, while the value obtained from the concentration change corresponding to the temperature drop showed 0.40 gram per 100 grams of solution. This is a good agreement.

It was found early in the work that when the rate of agitation of the solution, as well as the initial average temperature, was constant there was a definite relation between the amount of material crystallized out and the increase in surface as shown by the screen tests, for a given time of contact of crystals in the crystallizer.

The surface of the crystals in the product in run 15 is $\frac{119.3}{100} \times 4573.4 = 5465$ sq. cm. The surface of the seed crystals is $36.5 \times 81.61 = 2980$ sq. cm. The increase in weight, $\Delta W = 119.3 - 36.5 = 82.8$ grams. The increase in surface is $5465 - 2980 = 2485$ sq. cm. The rate of

$$\frac{\Delta W}{\Delta S} \text{ is } \frac{82.8}{2485} = 33.3 \times 10^{-3}$$

for a time of contact of 53.6 minutes. To determine the time of contact of crystals in the crystallizer the following observations were made. The volume of material in the tube was calculated to be 6600 cc. and the pump discharge was 126 cc. a minute for an average of the first part of the run. The time for the solution to pass through the crystallizer would then be $\frac{6600}{126}$, or 52.3 minutes. The observed value in the first part of this run for the crystals to appear in the salt leg was the difference in time between 11:12 A. M. and 10:20 A. M., or 52 minutes. That is, the crystals passed through the crystallizer at the same rate as the solution. The average time of contact for the whole run would then be $\frac{6600}{126}$, or 53.6 minutes.

It should be especially noted that in this apparatus small time of contact gives a high rate of change of concentration in the crystallizer or large driving force, while a large time of contact gives a low rate of change of concentration and a low driving force for the crystallization process. This is because a small time of contact means a rapid rate of circulation. Hence, if terminal conditions are kept constant, a rapid rate of flow gives a rapid rate of cooling.

Similar calculations were made for all the experimental data. The summarized data and results for both $Na_2SO_4 \cdot 10H_2O$ and $MgSO_4 \cdot 7H_2O$ are shown in Tables III and IV.

Results with $Na_2SO_4 \cdot 10H_2O$—For each run the value

Table III—Data for $Na_2SO_4.10H_2O$ at 27.11°, 29.26°, and 30.90° C.

(Agitator speed in all runs 9.5 r. p. m.)

Run	Satura-tion Temp.	Outlet Temp.	Av. Run Temp.	Flow	Time Contact	Yield per Hour	Seed Crystals per Hour	Screen Test of Product Per Cent on Each Screen							
								10	14	20	28	35	48	65	$\frac{W}{S}\times10^{-3}$
	° C.	*° C.*	*° C.*	*Cc. per min.*	*Min.*	*Grams*	*Grams*								
						AVERAGE TEMPERATURE 27.11° C.									
15	27.125	26.85	26.98	123	53.6	119.3	36.5	1.15	23.94	41.30	27.90	4.10	1.00	0.60	33.3
16	27.42	26.98	27.20	131	50.4	122.4	38.4	1.80	16.70	46.40	24.18	7.71	2.65	0.61	30.0
17	27.49	27.22	27.35	142	46.5	137.4	43.7	1.11	12.02	48.35	27.44	6.93	3.35	0.80	28.2
19	27.20	26.85	27.03	158	41 75	181.5	43.2	1.73	19.25	46.50	23 50	6.00	2.47	0.58	27.2
14	27.17	26.80	26.98	195	33.82	189.8	42.6	0.38	9.53	36.46	43.21	8.99	0.78	0.64	23.06
		Av. 27.11													
						AVERAGE TEMPERATURE 29.26° C.									
21	29.61	29.30	29.42	127	51.9	175.0	54.8	1.51	24.64	45.20	22.10	5.15	1.19	0.16	36.12
12	29.07	28.59	28.83	172	38.36	271.5	53.3	2.92	22.50	44.98	22.18	4.01	2.21	1.14	26.80
6	29.94	29.65	29.78	180	36.64	192.0	35.4	3.08	22.72	46.10	20.26	4.71	2.37	0.69	26.76
4	29.26	28.76	29.01	202	32.64	289.3	43.0	1.17	23.90	43.70	24.00	4.60	1.92	0.72	25.00
		Av. 29.26													
						AVERAGE TEMPERATURE 30.90° C.									
22	31.08	30 81	30 97	142.5	46.3	147.0	49.5	1.23	21.01	43.45	29.27	4.42	0.52	0.11	37.0
25	30.99	30.62	30 81	168	39 3	133.8	42.1	0.73	15.35	51.50	27.22	3.52	1.20	0.50	33.1
26	31.11	30.72	30.91	197	33.5	202.0	48.7	0.70	20.70	48.17	24.15	4.98	1.05	0.25	29.3
		Av. 30.90													

Table IV—Data for $MgSO_4.7H_2O$ at 31.62° and 29.25° C.
(Agitator speed in all runs 11.75 r. p. m.)

Run	Saturation Temp.	Outlet Temp.	Av. Run Temp.	Flow	Time Contact	Yield per Hour	Seed Crystals per Hour	Screen Test of Product—Per Cent on Each Screen							
								10	14	20	28	35	48	65	$\frac{W}{S}\times10^{-3}$
	° C.	° C.	° C.	Cc. per min.	Min.	Grams	Grams								
						Average temperature 31.62° C.									
36	32.10	31.45	31.77	145.6	45.4	114.2	53.1	2.29	9.80	31.40	48.60	6.85	0.68	0.33	46.5
30	32.14	30.72	31.43	150	44.0	125.8	47.6	3.92	20.06	36.12	35.92	3.44	0.28	0.27	48.15
31	32.11	31.07	31.58	184	35.9	124.0	47.6	0.84	16.56	37.06	41.35	3.48	0.37	0.39	42.10
34	32.11	31.33	31.72	232	28.46	124.9	54.6	0.50	5.63	34.32	51.10	7.49	0.48	0.44	37.2
		Av. 31.62													
						Average temperature 29.25° C.									
38	29.255	28.59	28.92	149	44.3	103.2	50.6	0.36	4.03	28.50	57.30	9.17	0.32	0.31	40.77
39	29.85	29.28	29.56	186	35.5	96.6	53.6	0.20	2.13	11.74	65.07	19.07	0.92	0.90	34.5
		Av. 29.25													

of $\frac{\Delta W}{\Delta S} \times 10^{-3}$ was calculated. For any average temperature and rate of stirring, the results decrease with decreasing time of contact. This indicates that the crystal size is larger the greater the time of contact. When the driving force is large—that is, when the time of contact is small—the surface energy is increased, more surface is generated, and the size of the crystals decreases.

Let $\frac{\Delta W}{\Delta S} = y$, and suppose y varies with t (where t is time of contact), so that

$$\frac{dy}{dt} = ky \tag{5}$$

Then
$$\frac{dy}{y} = kdt \tag{6}$$

and
$$\log_e = kt + C \tag{7}$$

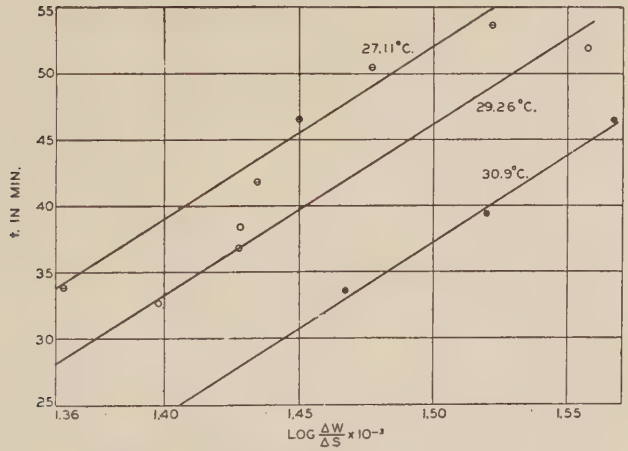

Figure 5—Crystallization Rate of Sodium Sulfate

If this equation holds, then a plot of log $\frac{\Delta W}{\Delta S}$ vs. t in minutes should give a straight line. The values plotted in Figure 5 show that this relation holds within ± 3 per cent at 27.1° C., as shown in Table V.

Table V—Comparison of Observed and Calculated Values for $\Delta W/\Delta S$ for $Na_2SO_4.10H_2O$ at 27.1° C.

Time of Contact	$\frac{\Delta W}{\Delta S} \times 10^{-3}$ Experimental	Calculated	Error
Minutes			*Per cent*
53.6	33.3	32.6	−2.1
50.4	30.0	30.8	+2.66
46.5	28.2	28.7	+1.77
41.75	27.2	26.4	−2.94
33.82	23.06	22.9	−0.69

The equation of this line at 27.1° C. is

$$\frac{\Delta W}{\Delta S} \times 10^{-3} = 12.57\ e^{0.0178t} \qquad (8)$$

In a similar way the results at 29.26° C. and at 30.90° C. were plotted (Figure 5) and found to obey the same law. At 29.26° C. the equation is

$$\frac{\Delta W}{\Delta S} \times 10^{-3} = 13.90\ e^{0.0178t} \qquad (9)$$

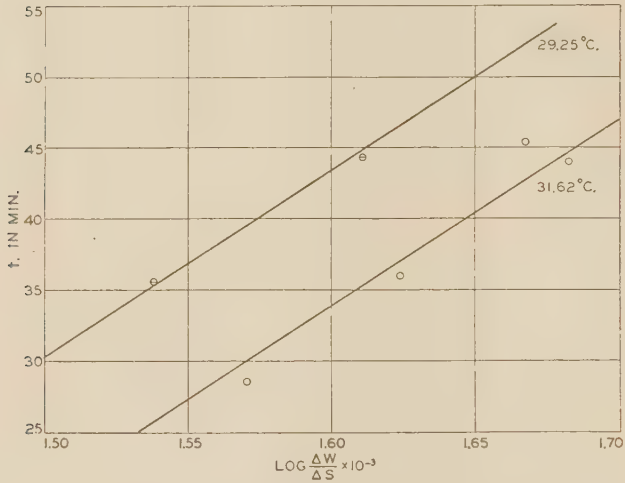

Figure 6—Crystallization Rate of Magnesium Sulfate

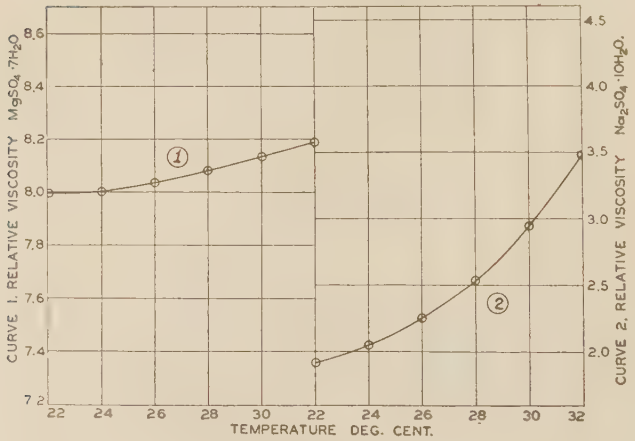

Figure 7—Relative Viscosity of Magnesium Sulfate and Sodium Sulfate

and at 30.9° C. the equation is

$$\frac{\Delta W}{\Delta S} \times 10^{-3} = 16.26\ e^{0.0178t} \qquad (10)$$

Results with $MgSO_4.7H_2O$—In order to confirm the applicability of this method to study of crystallization of

other salts, similar experiments were made with $MgSO_4.7H_2O$. This salt crystallizes in the rhombic system, the density of the crystals is 1.676, and the specific gravity and viscosity of its saturated solutions are higher than those of $Na_2SO_4.10H_2O$, which crystallizes in the monoclinic system, the density of the crystals being 1.462.

Similar results were obtained with $MgSO_4.7H_2O$ as the plot of time of contact against log $\frac{\Delta W}{\Delta S}$ shows in Figure 6. At 31.6° C. the equation for $MgSO_4.7H_2O$ is

$$\frac{\Delta W}{\Delta S} \times 10^{-3} = 22.13\ e^{0.0175t} \qquad (11)$$

and at 29.25° C. the equation is

$$\frac{\Delta W}{\Delta S} \times 10^{-3} = 18.52\ e^{0.0175t} \qquad (12)$$

These equations are all of the general form

$$\frac{\Delta W}{\Delta S} \times 10^{-3} = K\ e^{at} \qquad (13)$$

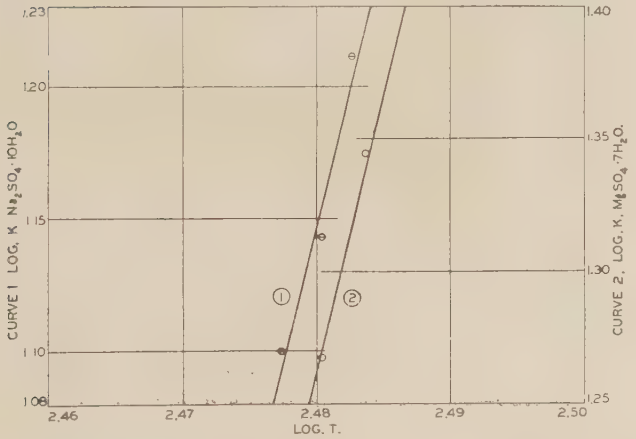

Figure 8—Effect of Temperature on Rate of Crystallization

Interesting relations were found between the values of K and the absolute temperature and between the values of K and the relative viscosities of the respective solutions.

The plot of log K vs. log T for both $Na_2SO_4.10H_2O$ and $MgSO_4.7H_2O$ is given in Figure 8. The authors realize that further data are needed to determine the slope of these lines but it is assumed that they may safely be used for interpolation over the experimental range of temperature. These results indicate that K increases with temperature.

With these salts the concentrations and also the viscosities of the saturated solutions increase with temperature.

The relative viscosities of these solutions were plotted from the data of Lampert and Montillon,[21] and are shown in Figure 7.

[21] Unpublished thesis, University of Minnesota.

A plot of log K vs. log relative viscosity is shown in Figure 9. These curves indicate the possibility that the variation of log K with T may be due in large part to the variations in relative viscosity, and the accompanying changes in concentration of the solutions and the changes in rate of diffusion of solution around the growing crystals. Further work is needed to clarify these relations and to determine the effect of rate of stirring, especially on the more viscous magnesium sulfate solutions.

DISCUSSION OF RESULTS

In the previous work done to determine the velocity of crystallization using a large number of small seed crystals as a starting point for the study of the rate of growth, the

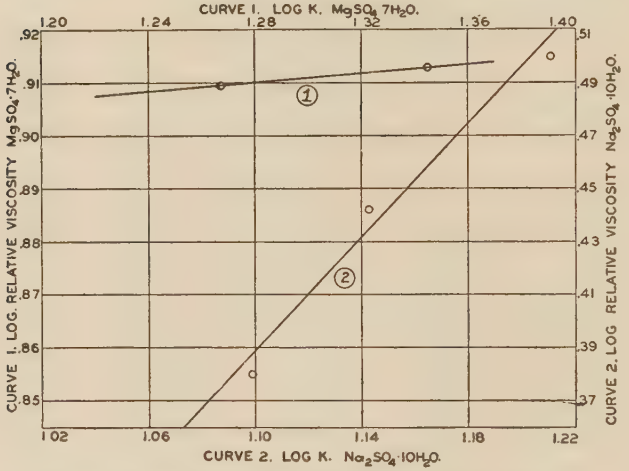

Figure 9—Effect of Viscosity on Rate of Crystallization

assumption has been made by Marc[22] and Jenkins[11] that these seed crystals all grow at the same rate. This assumption is questionable. The further assumption has been made that the ratio of the surfaces of crystals in any one time interval is proportional to the two-thirds power of the ratio of the weights of material for that same time interval. This assumption is also questionable. Work has been done on individual crystals in determining the ordinary velocity of crystallization which does not involve these assumptions because individual crystals were weighed and measured.

All the screen tests made in the course of this investigation showed that the seed crystals did not grow at the same rate, but that the general shape of a plot of percentage by weight of particles retained on any one screen against the corresponding average diameter for that screen was similar to that

[22] *Z. physik. Chem.*, **61**, 385 (1907).

of the ordinary probability curve (Figures 10 and 11). In each case the full lines represent the actual data, the upper curve being a cumulative per cent weight retained *vs.* screen mesh, the lower curve the direct plot for the same data. These curves are typical of all those obtained. In general, the maximum

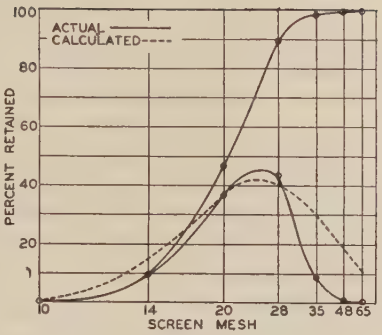

Figure 10—Screen Analysis of Product—Na_2SO_4, Run 14

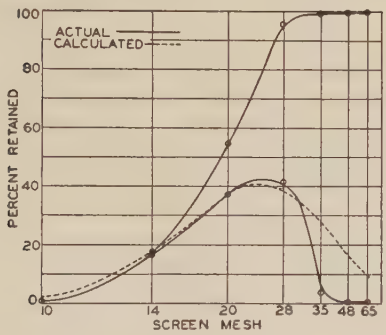

Figure 11—Screen Analysis of Product—$MgSO_4$, Run 31

weight on one screen is found about two sizes above the size of the seed crystals, which were 28- to 35-mesh material in each case.

Since the direct plot of percentage by weight of particles retained on any one screen against the corresponding average diameter for that screen was similar to the ordinary probability curve, it was decided to attempt to find an equation of general form which by comparison would show the facts as they exist.

It was found that an equation in the form

$$\frac{n}{b} = \frac{4}{\pi}\left(\frac{d}{a}\right)^2 e^{-\left(\frac{d}{a}\right)^2} \qquad (14)$$

where a and b are constants, d is the diameter of particle in centimeters, and n is the number of particles, agreed fairly well with the general distribution of sizes of the larger particles, but did not in any case agree with the actual number of small particles found, as shown by the dotted curves in both Figures 10 and 11. This indicates that there is a much smaller number of small particles than would be expected from a random distribution, and is in direct agreement with the viewpoint of Liveing,[23] who considers that, since larger amounts of energy are needed to generate new surfaces than to increase old ones, large crystals will add weight faster than smaller ones, for the ratio of increase of surface to that of volume decreases as the crystal grows.

The same view is also consistent with the thermodynamic

[23] *Proc. Roy. Inst. Gt. Brit.*, **13**, 250 (1891).

viewpoint as given by Lewis and Randall[24] in discussing surface energy, who conclude that the escaping tendency is greater, the smaller the radius of particle.

CONCLUSIONS

Mechanism of Crystallization—These results lead to the conclusion that the growing small crystals do not increase in size at the same rates, but those somewhat larger add weight faster than the smaller, giving a distribution of sizes in the final product which follows some unknown probability function but one in which the relation of increase in weight to increase in surface is definite, when the temperature and rate of stirring are constant, for a given rate of change of concentration.

Prediction of Screen Analysis of Product for Given Conditions—From the results obtained it will be shown that an approximate method of predicting the screen analysis of product under a given set of conditions is possible. At present only a limited amount of data is available, but after sufficient data are accumulated it will be possible to determine such an analysis quite readily. Such data will also materially aid the designer of crystallization apparatus.

Suppose that $Na_2SO_4.10H_2O$ is being crystallized from saturated solutions between 27° and 30° C. Assume that 40 grams of 35-mesh seed crystals are used per hour with a rate of flow of solution of 150 cc. a minute. The yield per hour will be taken at the average temperature of 30.9° C. and a change in concentration of 0.30 gram per 100 grams of solution will be assumed.

$$150 \times 60 \times 1.297 \times \frac{0.30}{100} \times \frac{322.2}{142.1} = 79.4 \text{ grams per hour}$$

increase in weight.

The total yield per hour is 79.4 + 40.0 = 119.4 grams. With a rate of flow of 150 cc. a minute, the time of contact is 44 minutes. The value of $\frac{\Delta W}{\Delta S} \times 10^{-3} = 16.10\ e^{0.0178t}$ from Figure 8 is

$$\frac{\Delta W}{\Delta S} \times 10^{-3} = 35.23 \text{ and } \frac{\Delta S}{\Delta W} = \frac{1}{0.03523} = 28.38$$

The surface generated under these conditions will be $79.4 \times 28.38 = 2252$ sq. cm. The initial surface was

$$\frac{40}{0.0503 \times 0.2436} = 3262 \text{ sq. cm.}$$

The total surface for the total product is 6514 sq. cm. for 119.4 grams.

Similarly, the surface of the final product could be figured for a second change in concentration over the next length of crystallizer. This would occur at 30.7° C. for the second 0.300 gram concentration change. Yield in grams would be

[24] "Thermodynamics," p. 251 (1923).

$$150 \times 60 \times 1.294 \times 0.3 \times \frac{322.2}{142.1} = 79.3 \text{ grams per hour}$$

At this temperature

$$\frac{\Delta W}{\Delta S} \times 10^{-3} = 15.91\, e^{0.0178t} = 34.84$$

and

$$\frac{\Delta S}{\Delta W} = \frac{1}{0.03484} = 28.70$$

Then $28.7 \times 79.3 = 2280$ sq. cm. The total is $6514 + 2280 = 8794$ sq. cm. for 198.7 grams, or 4420 per 100 grams of product. The average diameter would be

$$\frac{198.7}{D \times 0.2436} = 8794, \quad D = \frac{198.7}{8794 \times 0.2436} = 0.0928 \text{ cm.}$$

Approximate values for the first three screen sizes may be calculated by the aid of the probability equation:

$$n = \frac{4}{\pi}\left(\frac{d}{a}\right)^2 e^{-\left(\frac{d}{a}\right)^2}$$

where $a = \frac{1}{2}D\sqrt{\pi}$ or $a = \frac{0.0928}{2} = 0.0822$

For example, on 10 mesh

$$n = \frac{4}{\pi}\left(\frac{0.20066}{0.0822}\right)^2 e^{-\left(\frac{0.20066}{0.0822}\right)^2} \qquad n = \frac{4}{\pi} 5.99\, e^{-5.99} = 1.92$$

Similarly, 14- and 20-mesh values are figured.

Mesh	Opening	n	Screen Test		Area per Gram		Total Surface
	Cm.		*Per cent*		*Cc.*		*Cc.*
10	0.2006	1.92	2.0	×	20.46	=	40.8
14	0.1410	19.66	20.0	×	29.14	=	582.0
20	0.1000	42.80	43.0	×	41.03	=	1762.0
28			30.0[a]	×	57.73	=	1730.0
35			4.0[a]	×	81.61	=	326.0
							4440.8

[a] From actual tests 28-mesh material is about one-half that of 14 + 20 mesh, and the amount of 35-mesh is the remainder or 4 per cent.

The surface of the calculated product is within 1 per cent of the required and the amount on any one screen would be within a few per cent of the expected values.

Quantitative Data—It is very significant that quantitative measurements showing the relation between the weight of material crystallized and the new surface generated have been made and further that these results are consistent with each other, within a range of reasonable experimental error. Previous work in this field has been confined to a study of comparatively large individual crystals.